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XIX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

TURMEROL.

By C. Loring Jackson and W. H. Warren.

Presented October 12, 1892.

Some years ago one of us, in conjunction with A. E. Menke, described a compound obtained from the oily extract of turmeric, to which the name of turmerol was given.* The present paper contains some additional work on this substance, which we are obliged to publish in an unfinished state because the departure of one of us from Cambridge prevents us from continuing the work together.

The turmerol at the time of its discovery was purified by distillation *in vacuo*, but the method used was a very imperfect one, because at that time no description of the best methods now in use had come to our notice, if indeed they had been described at all. Accordingly when we returned to the subject we felt it was necessary to revise this part of the work, and for this purpose applied to the turmerol the excellent method of fractional distillation *in vacuo* contrived by Anschütz, and soon found that the preparation studied by one of us and Menke was impure, and therefore that the formula of turmerol needed correction. Our analyses of a sample carefully purified and proved to be homogeneous by the analyses of different fractions led to the formula $C_{13}H_{18}O$ or $C_{14}H_{20}O$. We have been unable to determine which of these is correct, because the difference between them is only 0.25 per cent for the carbon. This new formula agrees much better with the formulas of the oxidation products already obtained than that assigned to turmerol in the first paper on this subject.

The oxidation of turmerol with dilute nitric acid converted it into paratoluylic acid, which was identified by its melting point, 178°, the analyses of its calcium salt and anilid, and its conversion into terephthalic acid by further oxidation. This observation proves that turmerol contains a benzol ring with a methyl group attached to it, and a long side-chain of six (or seven) atoms of carbon in the para position to the methyl. In regard to the nature of the long side-chain we cannot speak with certainty, but it has been proved that one of the atoms of carbon in it is unsymmetrical, because turmerol shows circular polarization, and that the atom of oxygen is attracted to this side-chain. The earlier work of Menke and one of us further seems to indicate that turmerol is an alcohol,* and that it is oxidized by cold potassic permanganate with formation of acetic acid, carbonic dioxide, and two acids, $C_{11}H_{14}O_2$ (turmeric acid), and $C_{10}H_{12}O_4$? (apoturmeric acid).† We feel, however, that this earlier work needs revision before these points can be considered definitely settled, as the experiments on the alcoholic nature of turmerol are susceptible of an interpretation different from that given to them in the paper in which they were described, and the formula of apoturmeric acid is very doubtful. This revision will be undertaken in this Laboratory, it is hoped, during the coming year.

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* These Proceedings, XVIII. 8.

Although it would be easy to assign a provisional formula to turmerol in accordance with the facts already observed, we have thought it wiser to postpone doing this until further investigation has given us a more secure foundation for such a formula.

Purification and Analysis of Turmerol.

The crude turmeric oil extracted from ground Bengal turmeric with ligroine, as described in an earlier paper,‡ was heated to 150° under ordinary pressure for some time to remove as much as possible of the ligroine, and then distilled under a pressure of 11–12 mm. according to the method of Anschütz, carrying the temperature to 200°. This separated it into a small lower fraction containing ligroine, a larger one consisting principally of turmerol, and a viscous retort residue which formed about one half of the original oil. The large middle portion was repeatedly fractioned at a pressure of 11–12 mm., which divided it into a small lower fraction containing ligroine, an insignificant retort residue, and the principal amount boiling from 158° to 163° under 11–12 mm. pressure. To test the purity of this substance it was distilled under the same diminished pressure once more, collecting the product in three fractions, the first and last very small in quantity, the middle one containing most of the substance, and these three fractions were then analyzed with the following results: —

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* These Proceedings, XVIII. 11.

† These Proceedings, XIX. 215.

‡ These Proceedings, XVII. 112.

I. 0.3701 gr. of the lowest fraction gave on combustion 1.1215 gr. of carbonic dioxide and 0.3274 gr. of water.
II. 0.4331 gr. of the middle fraction gave on combustion 1.3071 gr. of carbonic dioxide and 0.3802 gr. of water.
III. 0.4795 gr. of the highest fraction gave on combustion 1.4469 gr. of carbonic dioxide and 0.4153 gr. of water.

	Found.		
	I.	II.	III.
Carbon	82.64	82.28	82.30
Hydrogen	9.83	9.75	9.62

This experiment showed that the substance was not perfectly pure, since the lowest fraction contained more carbon than either of those which came over at higher temperatures. Accordingly the distillation at a pressure of 11–12 mm. was repeated, removing each time only a very small fraction which came over first, until this small lower fraction gave on analysis the same result as the portion left in the boiling flask. This occurred after the third distillation, when the following results were obtained: —

IV. 0.3408 gr. of the small lowest fraction gave on combustion 1.0265 gr. of carbonic dioxide and 0.2963 gr. of water.
V. 0.3658 gr. of the principal fraction gave on combustion 1.1041 gr. of carbonic dioxide and 0.3175 gr. of water.

	Found.	
	IV.	V.
Carbon	82.13	82.28
Hydrogen	9.66	9.65

To these analyses we add another of an entirely different sample of turmerol.

VI. 0.5045 gr. of the substance gave on combustion 1.5246 gr. of carbonic dioxide and 0.4375 gr. of water.

The percentages of carbon and hydrogen obtained from the analyses of pure turmerol are collected in the following table: —

	II.	III.	IV.	V.	VI.
Carbon	82.28	82.30	82.13	82.28	82.39
Hydrogen	9.75	9.62	9.66	9.65	9.64

These results agree nearly with those calculated for the following formulas:—

	Calculated for	
	$C_{13}H_{18}O$.	$C_{14}H_{20}O$.
Carbon	82.10	82.35
Hydrogen	9.47	9.80

Of these we prefer the first, as this brings the calculated percentage of hydrogen below those found. On the other hand the percentages of carbon found are all a little too high for this formula, which may perhaps be due to the presence of a trace of ligroine. It is evident that it is impossible to decide with certainty from these analyses which of these formulas is the correct one.

Properties of Turmerol. — The turmerol, after the purification described above, forms a yellowish oil, with a peculiar rather agreeable odor. It is decomposed partially by distillation at ordinary pressure, but under a pressure of 11–12 mm. it distils unchanged between 158° and 163°. Its specific gravity at 24°, referred to water at 4°, is 0.9561. Turmerol acts upon polarized light, turning the ray toward the right, with the following specific rotation for sodium light:

$$[\alpha]_D = 24^\circ.58.$$

It mixes easily with the common organic solvents, but is insoluble in water.

Oxidation of Turmerol with Nitric Acid.

In a previous paper[*] one of us with A. E. Menke showed that turmerol, when oxidized in the cold with potassic permanganate, gave in addition to carbonic dioxide and acetic acid two new acids, to which the names turmeric acid and apoturmeric acid, and the formulas $C_{11}H_{14}O_2$ and $C_{10}H_{12}O_4$? were assigned. As in this work the characterization of the apoturmeric acid was far from satisfactory owing to the very small yields and the unmanageable nature of these acids and their salts, and as we hoped by further study of these substances to throw light on the constitution of turmerol, we took up this part of the subject again. Since the preparation and purification according to the methods used in the earlier work were tedious in the highest degree, we tried the action of dilute nitric acid on turmerol in the hope that this might lead us more quickly to the desired result. This did not prove to be the case, but the product obtained was quite as important as the two acids we had hoped to get.

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[*] These Proceedings, XIX. 215.

We proceeded as follows. A convenient quantity of turmerol was boiled with nitric acid (one part of acid of 1.38 specific gravity diluted with two parts of water) under a reverse condenser for some time. The yellow solution was filtered hot, and on cooling deposited a white crystalline substance which sublimed very easily at a little over 170°. It was purified by sublimation, followed by warming with tin and hydrochloric acid to remove any nitro compound which might have been formed; after this it was crystallized from boiling water until it showed a constant melting point, which stood at 178°. This at once suggested that the substance was the paratoluylic acid $CH_3C_6H_4COOH$, which melts according to Beilstein and Yssel * at 176° to 177°, according to Fischli † at 180°. To confirm this inference we analyzed the calcium salt with the following results: —

I. 0.1106 gr. of the air-dried salt lost 0.0165 gr. when dried at 140°.
II. 0.1212 gr. of the air-dried salt lost 0.0176 gr. when dried at 140°.

	Calculated for $(C_8H_7O_2)_2Ca \cdot 3H_2O$.	Found. I.	Found. II.
Water	14.83	14.92	14.52

0.2848 gr. of the calcium salt dried at 140° gave 0.1246 gr. of calcic sulphate.

	Calculated for $(C_8H_7O_2)_2Ca$.	Found.
Calcium	12.90	12.86

The amount of water found (three molecules) corresponds to that obtained by Beilstein and Yssel * in the calcium salt of paratoluylic acid. We also converted the acid into its anilid by treating it successively with phosphoric pentachloride and aniline. This after repeated crystallization from dilute alcohol melted constant at 143°, and gave the following result on analysis: —

0.1122 gr. of the substance gave 7 c.c. of nitrogen at a temperature of 29° and a pressure of 753.7 mm.

	Calculated for $C_8H_7ONHC_6H_5$	Found.
Nitrogen	6.63	6.75

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* Ann. Chem., CXXXVII. 302.
† Ber. d. ch. G., XII. 615.

Here again the analysis gave the desired result, but our anilid melted at 143°, whereas according to Fischli * the anilid of paratoluylic acid melts at 139°, according to Brückner † at 140–141° ; we felt, therefore, that further proof of the para position of the side-chains in our acid was necessary, and this we obtained by the oxidation of the acid with potassic dichromate, according to the directions given by Beilstein and Yssel. For this purpose 0.5 gr. of our acid was boiled in a flask with a return condenser with four parts of potassic dichromate, and an excess of sulphuric acid diluted with twice its volume of water, until there was a copious white precipitate; this was then filtered out, boiled three times with water, and the residue converted into its dimethylester, which melted at 140–141°, thus proving that the product was terephthalic acid, and that our acid was the paratoluylic acid. We may add that a certain amount of terephthalic acid was always obtained with the paratoluylic acid when we oxidized turmerol with dilute nitric acid.

Some unsuccessful attempts to make derivatives of the turmerylchloride, which was described in a previous paper,‡ may be mentioned here. The chloride was made by heating phosphorous trichloride with turmerol for three hours. The product was purified by washing its ethereal solution with dilute sodic hydrate and water, drying with calcic chloride, and distilling off the ether. It formed a dark oil, with a smell very different from that of turmerol, but, as it decomposed even when distilled at a pressure of 12 mm., no attempt was made to analyze it again. In the hope of obtaining an aldehyd or ketone from it, 10 gr. of the chloride were boiled with an aqueous solution of plumbic nitrate. Some plumbic chloride was formed, but the quantity of chlorine removed was only 0.2363 gr., whereas the amount calculated for the complete reaction was 1.868 gr.; we obtained therefore only 12.65 per cent of the calculated amount, and, as the reaction was so incomplete, it is not surprising that we were unable to isolate the organic product. We also tried the action of potassic phthalimide on the turmerylchloride in the hope of getting a turmerylamine, but found there was no action at 100°, little or none at 150°. From these results it is evident that turmerylchloride is not a very reactive substance.

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* Ber. d. ch. G., XII. 615.

† Ann. Chem., CCV. 132.

‡ These Proceedings, XVIII. 11.